

PHOTO-ELECTROCHEMICAL REACTIONS IN SOLUTION

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The apparent similarity between photolytic and electrolytic processes in solution has prompted recent work combining photochemical and electrochemical techniques (1,2). Two objectives can be discerned: First, chemical transients present in photolytic processes can be generated electrolytically under accurately controlled conditions, and their subsequent chemistry studied. The results of these studies can be used to interpret photochemical data.

A second objective in this work is to use electrochemical techniques as a means of monitoring transient photolytic species during a photochemical process. Several analytical advantages are obtained in this way: sensitivity is available for dilute concentrations of a wide range of compounds; nearly the same detection limit exists for all electroactive compounds; and time resolution in the microsecond range is available.

The flash photolysis technique was used in this work to initiate the photochemical processes. A Xenon flash lamp (XFX47A, Edgerton, Germeshausen & Grier, Inc., Boston, Mass.) was employed, and flash times of the order of 5 to 20 microseconds were obtained with about 100 joules of U.V.-visible radiant energy. Potentiostatic measurements of transient photolytic products were made using a simple fast-rise potentiostat employing Philbrick SK2-V and SK2-B operational amplifiers (Philbrick Researches, Inc., Dedham, Mass.). A hanging mercury drop electrode was used as the working electrode, and was placed in solution in the region of greatest photolytic activity. (The flash lamp itself was partially immersed in solution.)

Results and Discussion

The specific objectives of the work reported here were, one, to follow very rapid photolytic reactions; two, to study photochemical processes where the electrochemical characteristics had not been well-evaluated previously; and, three, to evaluate the electrochemical characteristics of electronically excited species.

In order to accomplish the first objective, two instrumental problems had to be solved. The electronic instability in the potentiostat generated by the flash lamp discharge had to be eliminated; and the time resolution (rise-time) of the potentiostat had to be optimized. In addition, the time-delayed potentiostatic method developed previously (2) had to be modified in order to obtain kinetic data for photolytic processes with half-lives less than 1 msec.

The initial potentiostat instability was traced to the flash lamp triggering technique which had improperly resulted in an extraneous arc discharge in the trigger circuit. This arc discharge, when coupled to the overall potentiostatic circuit, resulted in a loss of potential

control lasting from 50 to 2000 microseconds. This problem was solved by imposing directly to the flash lamp a voltage sufficient to cause its self-discharge. With this approach, negligible initial potentiostat instability was obtained.

Fast time resolution was obtained by employing a single-amplifier potentiostat with greater than 1 MHz band pass, coupled with an electrolysis cell design minimizing uncompensated and total cell resistance (3).

One chemical system chosen for study was benzophenone in 80% ethanol, at pH's from 7 to 13, where the dimerization of the photo-produced free radical occurs very rapidly. This system provided a real test of the time-resolving capabilities of the instrumentation.

The second objective mentioned above, to demonstrate the applicability of the overall photo-electrochemical technique for processes where the electrochemistry was not well-defined, was accomplished by selecting two other systems for study: the photoreduction of Fe(III) in oxalate medium, and the photoreduction of methylene blue. Although the general polarographic characteristics of these systems were well known, the nature of transient intermediates in the overall electrode process had not been characterized. Thus, rapid cyclic electrochemical investigations were carried out with these systems. Cyclic voltammetry and cyclic potential-step electrolysis were used with frequencies up to 50 kHz. The semiquinone radical ion intermediate in the methylene blue reduction process was observed in both the photolytic and electrolytic experiments. The kinetics of its chemical decomposition were measured from both electrochemical and photochemical studies.

Elucidation of the Fe(III)-oxalate system involved similar electrochemical studies. However, a separate study of the electrochemistry of oxalate was necessary in order to interpret photo-electrochemical data.

The electrochemical detection of excited species has not been conclusively verified in our work as of this writing. However, experimental studies are continuing along these lines. The triplet state of methylene blue, for example, has a life-time of the order of 100 microseconds; and, with the present time resolution of the photo-electrochemical technique, its electrochemical characteristics ought to be discernible.

Literature Cited

1. Berg, H., Z. Anal. Chem., **216**, 165 (1966).
2. Perone, S. P., and Birk, J. R., Anal. Chem., **38**, 1589 (1966).
3. Perone, S. P., Ibid., 1158.